REVIEW OF ENVIRONMENTAL SUITABILITY OF SCRAP TIRES

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1. INTRODUCTION

Since rain water will percolate through earth structures constructed with shredded tires, concern exists regarding the potential for leaching of organic and inorganic constituents. Tires contain numerous ingredients such as carbon black, vulcanizing agents, metallic reinforcements, antioxidants, pigments, accelerators (Miller and Chadik 1993) and may also contain petroleum residues obtained through use. Thus, leaching studies have focused on both organic and inorganic compounds. Table 1. summarizes the studies conducted on tire leachate characteristics.

2. POTENTIAL CONTAMINANTS REPORTED IN THE LITERATURE

2.1 Organic Compounds

A study prepared for the Minnesota Pollution Control Agency (MPCA) (1990) indicates that under alkaline conditions, the concentration of polynuclear aromatic hydrocarbons (PAHs) leached from tire chips exceeds drinking water standards. PAHs may leach from carbon black, recipe extenders (Miller and Chadik 1993), or petroleum residues.

The second class of potential contaminants includes nitrogen and sulfur containing organic compounds which form the basis of vulcanizing agents, anti-oxidants, and/or accelerators. Volatile organic compounds (VOCs) are used in tire

Research	Reference	Type of Tire	Type of Study	Variables	Leachate Analysis	Results
Tire Chip Evaluation Permeability and Leachability Assessments	Waste Management of Pennsylvania (1989)	Tire Chips	Column testing with leachate	Temp 23°C, 50° C Analysis at 0, 30, 60, 90 days	pH, sulfides, cyanides, EPA tox- metals	No appreciable change in concentration in 90 days
TCLP (Toxicity Characterization Leaching Procedure) Assessment Project	Rubber Manufacturers Association (RMA 1990)	Shredded tires (new)	Batch Tests	Leaching Sol. pH 4.9, pH 2.9 cured, uncured ground, unground	Volatiles, semi-volatiles, metal ions	None of the samples exceeded TCLP levels
Environmental Study of the Use of Shredded Waste Tires for Roadway Subgrade Support	Minnesota Pollution Control Agency (1990)	Shredded Tires (new, old)	Laboratory and field test	pH 3.5, 5, 7, 8	14 metal ions, hydrocarbons	Drinking water standards were exceeded under worst case conditions, but EP- toxicity limits were not exceeded. Field tests were not reliable.
Evaluation of the Potential Toxicity of Automobile Tires in the Aquatic Environment	Environment Canada National Water Institute (1992)	Whole tires (breakwater, old, new)	Effect of tire leachate on fish and <i>Daphnia</i>	time, 5, 10, 20, 40 days	Toxicity analysis on living organism	Substances contributing to toxicity are water soluble and persistent.
Development of Engineering Criteria for Shredded Waste Tires in Highway Applications	Edil and Bosscher (1992)	Shredded tires (old)	Lab (AFS leach & EP-toxicity) test, field samples (lysimeter under embankment fill)	Samples taken 10 times in 2 years in the field	Metal ions, water quality index tests (pH, alkalinity, BOD,COD etc.)	Slight alkaline conditions but no specific health concern. Field samples were affected from other sources. Laboratory samples leached Ba, Fe, Mn, and Zn but leachate showed no likelihood of hazardous levels
A Study of Waste Tire Leachability in Potential Disposal and Usage Environments	Miller and Chadik (1993)	Shredded tires (old)	Lab (batch) test, field samples (septic tank drain fill field)	Shred size, pH 5.4, 7.0, 8.6, time	Semi-volatiles, volatiles, metal ions	Metal ions, VOCs (benzene, toluene) and semi-volatiles leached. Biological activity may have affected results.
Water Quality Testing For Dingley Road Tire Chip Test Project	Humphrey and Katz (1995)	Shredded tires (old)	Field samples (monitoring wells near tire chip embankment)	15 cm and 30 cm thick tire chip layer above groundwater table	Metal ions, water quality index tests (pH, alkalinity, BOD,COD etc.)	All substances (except Mn) had concentrations below drinking water standards.
Analysis of Leachate from Column Tests of Soil-Tire Chip and Soil	Kim (1995)	Shredded tires (old)	Column tests	Soil-Tire Chips (830 days) Soil (790 days)	Metal lons Zn, Pb, Ba, As, Se	No sample exceeded drinking water limits in terms of metal concentration.

Table 1. Studies on Leaching from New and Scrap Tires.

manufacturing for mixing the rubber, promoting elasticity, and producing stickiness. Although most VOCs are driven off during the curing process, approximately 8% of total VOCs used in rubber manufacturing remain in the tire (Miller and Chadik 1993).

Miller and Chadik (1993) present results of a laboratory analysis of organic compounds. They conclude that aromatic components of gasoline (e.g., ketones), carboxylic acids, and aniline can be leached from tire shreds. Several other volatile compounds such as benzene and toluene were also present in their leachate. In a field study conducted by Miller and Chadik (1993), however, benzene was not found in the leachate. Toluene was found in the field leachate at low concentrations, and trimethylbenzene and 3-ethyltoluene were present in significant concentrations.

A study for the Rubber Manufacturers Association (RMA) (1990) indicates that volatile organics such as toluene, carbon disulfide, and methyl ethyl ketone may leach from tire chips. However, benzene was not detected in any samples. Only phenol was detected as a semi-volatile compound. The concentrations of organic compounds are below TCLP (Toxicity Characterization Leachability Procedure) limits.

Edil and Bosscher (1992) report biological (BOD) and chemical oxygen demand (COD) as indicators of organic compounds in leachate collected in their laboratory and field studies in Wisconsin. They report that laboratory tests show decreasing BOD and COD with time (Grefe 1989). In the field, however, they could not determine whether organic compounds in the leachate were generated by percolation through the tires or from surrounding soil.

2.1 Inorganic Compounds

Steel belts which become exposed during shredding are also a potential source of contamination. The Minnesota Pollution Control Agency (1990) tested for the presence of 14 metals in tire chip leachate. The laboratory test program concentrated on "worst case" conditions (in this case low or high pH conditions); USEPA's method SW-846 was used for sampling and handling procedures. The study reports that silver and mercury were not detected in any tests, whereas selenium, arsenic, calcium, iron, zinc, and chromium were detected. Depending on the test condition (e.g., pH), the concentration of some metals (barium, cadmium, chromium, lead, selenium, and zinc) exceeded Minnesota's Recommended Allowable Limits (RALs) for drinking water.

Grefe (1989) reports that zinc, barium, iron, and manganese were detected in their laboratory leachate tests (AFS-American Foundry Society test and EP-toxicity test). Concentrations of iron and manganese were above or at drinking water standards, whereas concentrations of zinc and barium were below drinking water standards. Edil and Bosscher's (1992) field test showed no significant leaching of barium or lead, but possible leaching of zinc and manganese. They indicate that leaching of zinc, manganese, and iron may also have occurred from the surrounding soil. Their field data showed high concentrations of cationic index parameters, such as conductivity, hardness, and calcium and magnesium concentrations, which may be due to leaching through the soil from activity at the site, such as roadway dust treatment.

Field study performed by Humphrey and Katz (1995) reported concentrations of barium, cadmium, chromium, copper, lead, and selenium that were lower than drinking water standards. Their field samples were taken 3 times in 28 months from groundwater monitoring wells installed in the vicinity of a tire chip roadway embankment. Only manganese was found at concentrations above drinking water standards in three of the wells adjacent to tire chip sections and the control well. Humphrey and Katz (1995) also explained the higher cationic index parameters as the result of the dust treatment in the summer and deicing treatment in the winter.

Miller and Chadik (1993) report that zinc and arsenic were found in their laboratory leaching tests at concentrations below drinking water standards. Low concentrations of chromium were also detected. They also pointed out that biological activity, co-precipitation, or the common ion in the leachate may make evaluating leaching of metals from tire chips complex.

The RMA (1990) study indicates that no silver, cadmium, and selenium exist in tire chip leachate. However, barium, chromium, and lead may leach at low concentrations that do not exceed TCLP limits.

Kim (1995) reports on an analysis of tire chip leachates that were obtained from column tests. Leachate samples were collected 830 days and 790 days after initial exposure from columns containing tire chips and soil or soil only. Filtered and unfiltered leachate samples were analyzed. Tap water was also tested for control purposes. Analyses were conducted for metals such as zinc, barium, arsenic, lead, and chromium. None of the samples had concentrations exceeding drinking water standards. However, unfiltered leachate from the column tests conducted with tire chips had higher concentrations of zinc and barium than the unfiltered leachate from the column containing soil only. Also, arsenic was found in higher concentrations in the unfiltered and filtered leachate from the soil-only tests. Lead was found in the highest concentration in the unfiltered leachate from the soil-tire chip tests. Filtered samples usually resulted in low metal concentrations. Differences in the metal concentrations in samples from different specimens may also be due to the different sampling period (i.e. 830 days for the soil-tire chip test and 790 days for soil only tests).

3. TEST METHODS

Batch tests are usually used to determine the leaching characteristics of tires. The mass of tires, extraction liquid, and volume of the container vary from study to study, even when standardized procedures like TCLP (Toxicity Characterization Leachability Procedure EPA, 1986) are used. With a few exceptions (Waste Management Pennsylvania 1989, Kim 1995), the experimental focus has been on leaching under stagnant conditions, which is not realistic. For example, a tire chip embankment partially submerged in groundwater is not in a stagnant condition. In a more realistic condition, liquid in the pores of a tire chip mass is diluted by the flowing groundwater.

Although the analytical equipment is usually the same for each study (e.g., gas chromatrography for organics or spectrometry for inorganics), procedures for sample handling and the detection limits vary. Handling and detecting organic compounds requires more attention than is required for inorganics. In addition, the precision of measurements at the parts per billion (ppb) level is questionable in most of the cases.

3.1 TCLP and EP-Toxicity Tests

The TCLP is normally used to determine if a waste material is hazardous. In the TCLP, the type and size of container and the extraction liquid are defined. The container has zero head space and a volume of 500-600 mL. Two types of extraction liquid are recommended, having a pH of 4.93 and pH of 2.88. The minimum amount of solid placed in the extractor is 100 grams for a non-volatile compound analysis or 25 grams for a volatile compound analysis. The study by the RMA (1990) used 600 g of tires in the TCLP. The time period for leaching is 16 hours in the TCLP.

The EP-Toxicity test (Extraction Procedure Toxicity Test), which was developed before TCLP, is also used for classifying a waste material as hazardous. EP-toxicity differs from TCLP because it specifies a 24-hour leaching period, no standard size extractor, and a pH of 5.0. The RMA (1990) compared leaching

results from TCLP and EP-toxicity tests and found that there was no significant difference between the EP-toxicity and TCLP results. In the RMA (1990) study, 300 grams of tire chips were used in the EP-toxicity test.

3.2 Batch Tests

The MPCA (1990) used batch tests. In their study, the container volumes and weight of the tire chips varied. However, in the report, concentrations were normalized with respect to the weight of tire chips in the containers, providing a basis for comparing different concentrations of leachate.

Miller and Chadik (1993) used 20 L polyethylene carboys with approximately 15 kg of tire chips, even though plastic containers can sorb or leach chemicals. The American Foundry Society batch test was used by Grefe (1989). In Grefe's study, tire chips were leached using distilled water at a liquid to solid mass ratio of 5:1.

3.3 Column Tests

Waste Management of Pennsylvania (1989) investigated tire chip leaching in column tests (20.3 cm diameter and 121.9 cm long) with leachate flowing at a percolation rate of 5.8 cm/day. Kim (1995) used steel containers (61 cm diameter and 91.4 cm long) for column testing of soil and tire chips. In Kim's study, the influent reservoir containing the tire chips (5 to 10 kg) had a volume of 170 L.

4. FACTORS AFFECTING LEACHATE CHARACTERISTICS

Factors that can affect the characteristics of leachate from tire chips include the aquatic environment in which the tire is exposed, the age of the tire chips, the size of the tire chips, and the time period that the tire chips are exposed to water.

4.1 Aquatic Environment/pH

The aquatic environment is described by the chemical characteristics of the solution, such as pH. MPCA (1990) investigated how acidic and alkaline environments affect tire chip leachate. Four different leaching tests designed to simulate a range of pH conditions (pH 3.5, 5.0, 7.0, 8.0) were performed. It was concluded that the highest concentration of metal ions (such as calcium, iron, and magnesium) occurred at a pH of 3.5. At this pH, cadmium, chromium, selenium, and zinc from old tire chips exceeded Minnesota RALs for drinking water. Leachate from new tire chips contained zinc, arsenic, and cadmium at concentrations exceeding the RALs when the solutions had a pH of 3.5 or pH of 5.0. However, none of the leachate samples exceeded the EP-toxicity criteria, which are used for classifying wastes as hazardous. It was also reported that slightly alkaline conditions (pH=8.0) resulted in the highest concentration of hydrocarbons.

Miller and Chadik (1993) prepared slightly acidic (pH=5.4), neutral (pH=7.0), slightly alkaline (pH=8.6) solutions to investigate how pH affects leachate characteristics. They also reported pH changes during the test, which were attributed to microbial enzymatic activity. They did not have a strong correlation between pH and the concentration of metal ions in the leachate. They proposed a possible reaction mechanism resulting in adsorption of metal ions by tire chips.

Edil and Bosscher (1992) report that tire chip leachates are slightly alkaline (pH =7.13 to 7.43), based on their field test results. They also recommend not using tire chips in highly acidic or alkaline environments to avoid generating stronger leachates.

4.2 New vs. Scrap Tires

Leachate from new tires may also contain inorganic and/or organic compounds. The leachate study on new tires prepared for the RMA (1990) found that leachate from new tires contains inorganic and organic compounds, but none of the concentrations exceed TCLP levels. MPCA (1990) indicates that newer tires contain slightly higher concentrations of leachable PAHs (new tires=1.2 ppb, old tires=0.6 ppb).

The Canada National Water Research Institute (1992) reports that new tires are also toxic to rainbow trout as scrap tires, which suggests that toxicity is associated with materials present in or on the rubber as a result of manufacturing process as opposed to being picked up later, when the tires are used or after they have been discarded. Toxicity concentrations of scrap tires, however, were found higher than those of new tires.

4.3 Tire Chip Size

Due to their larger surface area, it is expected that tire chips generate stronger leachates than whole tires. Miller and Chadik (1993) report that leachates from medium and large chips had higher concentrations of benzene (215 ppb and 253 ppb) than leachates from small chips (62 ppb). They also report that ethylbenzene, xylenes, and 2-ethyltoluene were found in approximately the same concentration regardless of chip size. They conclude that the effect of chip size is specific to each compound detected. However, they also report that higher or lower concentrations of a particular compound from smaller chip sizes can be due to variability in test samples. The study prepared for RMA (1990) indicates that leachates from ground and unground tires are comparable.

4.4 Immersion Time

The Canada National Water Research Institute (1992) investigated the toxicity of leachate generated by 5, 10, 20, or 40 days of exposure to tires on rainbow trout. Contaminants leached from tires reached lethal toxic concentrations for rainbow trout within 5 days. Afterwards, no appreciable change in concentration occurred in 40 days. Waste Management of Pennsylvania (1989) indicates that no significant change in leachate concentrations throughout a 90 day exposure period. Miller and Chadik (1993) report that benzene concentrations in laboratory leaching tests are highest at the beginning of a test and decrease rapidly and exponentially with time. In contrast, they found that toluene concentrations were initially low and then increased slowly with time. Miller and Chadik (1993) also report that the zinc concentration continually increased for 63 days and thereafter decreased.

Edil and Bosscher (1992) also report time-dependent composition of leachate collected in lysimeters underneath their shredded tire embankment. They attributed the changes to construction activities, such as roadway dust treatment

with calcium chloride and asphalt paving. Humphrey and Katz (1995) indicate that the time since construction (28 months) may be too short for substances to migrate from the tire chips to their monitoring wells. However, there was no significant increase in the concentrations of metal ions at three sampling dates and even some of the metals had lower concentrations at the last sampling date (e.g., Zn concentration decreased from <0.01 mg/L to less <0.003 mg/L for unfiltered samples taken from the vicinity of tire chip embankment). In addition, leachate from tire chips can be diluted when it mixes with groundwater.

4.5 Microbial Activity

Miller and Chadik (1993) report that gas was produced in several of their laboratory containers after 180 days of immersion. They also observed that attempts to maintain a constant pH using a buffer solution failed, which is indicative of a biological decomposition process (Miller and Chadik 1993). However, because Miller and Chadik (1993) performed no microbial analyses, there are no data to confirm their hypothesis.

The MPCA (1990) indicates that it is not necessary to investigate biological activity in scrap tires because the vegetation survey they performed in the field showed no difference between vegetation in waste tires and in background areas. The lack of a difference in vegetation indicates that off-gases generated by biological activity in scrap tires are not significant.

Kim (1995) observed gas formation in columns containing soil-tire chips and soil only, indicating possible biological activity. Gases formed a few months after starting the tests. Methylene chloride dissappeared in a few months in the tanks.

5. EFFECT OF LEACHATE ON GROUNDWATER

Several studies have been conducted to asses how metal ions, VOCs, and semi-volatile organic compounds leached from tire chips under worst case scenarios (such as acidic and alkaline conditions) affect groundwater quality. When tire chips are used as fill in earthwork construction, however, such extreme conditions are not likely to exist. Most often, tire chips are exposed to groundwater or percolating rain water. Thus, leachate from aqueous solutions that simulate groundwater or rainwater (or actual groundwater or rainwater) should be considered when investigating groundwater impacts.

The Minnesota Pollution Control Agency (1990) used a field test to determine how groundwater characteristics changed when exposed to tires. Concentrations of inorganic and organic compounds in groundwater samples collected under tire chip stockpiles were compared to concentrations in groundwater samples. Groundwater samples collected from Floodwood, Minnesota showed that zinc concentrations increased from less than 0.1 mg/L (background) to 0.87 mg/L (tire chips), iron concentrations increased from 5.8 mg/L to 298 mg/L, and magnesium concentrations increased from 6.2 mg/L to 383 mg/L. In contrast, the concentration of petroleum hydrocarbons decreased from 11.8 mg/L (background) to less than 0.5 mg/L (tire chips). This may indicate that hydrocarbons can be removed by tires if a concentration gradient exists between the tire and the surrounding environment. The study also indicates that samples collected beneath stockpiles at the Floodwood site exceeded Minnesota RALs for barium, cadmium, chromium, and lead while background samples did not exceed RALs. Soil samples taken from the area have concentrations of arsenic, barium, calcium, and selenium higher than in background samples. In contrast, aluminum, iron, magnesium, and zinc were found in lower concentrations.

Two of the nine laboratory test solutions that Miller and Chadik (1993) evaluated can be considered similar to groundwater in terms of pH (slightly alkaline) and total dissolved solids (< 1321 mg/L). In these solutions, the benzene concentration was as high as 0.0115 mg/L. Toluene had the highest concentration among other organic compounds (0.112 mg/L). Although the most predominant metal ions were zinc and arsenic, their concentrations were 4.25 mg/L and 0.008 mg/L, respectively, which are lower than drinking water standards.

Humphrey and Katz (1995) installed six groundwater monitoring wells in the vicinity of a tire chip embankment to investigate the change in groundwater quality due to tire leaching. They found no relationship between concentrations of metal ions in samples from the control well and the other wells. Sometimes, the concentrations from the control well were higher than the other wells (e.g., the zinc concentration was 0.01 mg/L in the control well and 0.004 mg/L in a well close to the tire chip embankment).

6. SYNTHESIS AND CONCLUSION

No leaching study in the literature yielded concentrations of inorganic and organic compounds that exceed TCLP and/or EP-toxicity limits. However, some of the inorganic compounds (e.g., Zn, Fe, Ba, Mn etc.) were found in concentrations higher than drinking water standards. Variability in the type of test setups, amount of tire chips and extraction liquid make the comparison among literature findings difficult, even though some tests were performed following standard procedures (e.g., TCLP). Converting leachate concentrations and the concentrations of different standards [TCLP, USEPA's Recommended Maximum Contamination Level (RMCLs), and Wisconsin's Groundwater Preventive Action Limits (PALs)] from the mass of compound per volume of liquid to the mass of compound per mass of tire chips, helps to compare the findings. Such a comparison is presented for laboratory studies in Table 2.

Two studies (RMA 1990, Miller and Chadik 1993) identified organic compounds that may exist in the tire leachate. The concentrations of toluene and phenol exceed Wisconsin PALs, but not RMCLs or TCLP limits. Although Miller and Chadik (1990) report high benzene concentrations (nearly twice the TCLP limit for benzene), the RMA (1990) study indicates no existence of benzene in the tire leachate.

Analysis of inorganic compounds is easier than organics and thus is performed in almost every study in the literature. Zinc, iron, barium, manganese, selenium, lead, chromium, and cadmium were found at concentrations higher than the RMCLs and Wisconsin PALs in most studies. Zinc and iron (two compounds

Table 2. Compounds in Tire C	hip Leachates.
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	Concentration Limits based on Tire Chip Mass			Reported Concentrations based on Tire Chip Mass				
Compound	TCLP ¹ (mg/kg)	USEPA's RMCLs ² (mg/kg)	WI PALs ² (mg/kg)	Grefe ³ (1989) (mg/kg)	RMA ³ (1990) (mg/kg)	MPCA (1990) (mg/kg)	Miller and Chadik ⁴ (1993) (mg/kg)	Kim⁵ (1995) (mg/kg)
As	25.9	0.06	6.15 x 10⁻³		-		0.02	
Ва	518.0	2.27	0.25	0.55	0.1	1.08		0.37
Cd	5.18	6.15 x 10⁻³	1.23 x 10⁻³		-	0.27		
Cr	25.9	0.15	6.15 x 10⁻³		0.008	0.51		0.019
Pb	25.9	0.025	6.15 x 10⁻³	0.075	0.003	0.92		0.14
Fe		0.37	0.18	1.15		1081		
Mn		0.06	0.03	1.5				
Zn		6.15	3.1	3.15		50.3	5.02	1.13
Se	5.18	0.055	1.23 x 10 ⁻³			0.44		0.05
Hg	1.03	3.7 x 10 ⁻³	2.5 x 10 ⁻³		7.2 x 10 ⁻⁵			
NO ₂ -NO ₃		1.23	2.46	1.85				
Toluene	333.79	2.46	84.3 x 10 ⁻³		0.034		0.28	
Carbon Disulfide	332.64				0.012			
Phenol	332.64		1.23 x 10 ⁻³		0.01			
Benzene	0.36	6.15 x 10 ⁻³	0.08 x 10 ⁻³		-		0.63	

¹TCLP are converted to mass of compound per kg of tire chips assuming that 100 g of tire chips with a specific gravity of 1.22 is used. (Volume of extractor= 600 mL, Mass of Solid= 100 grams for inorganics and 25 grams for volatile organics)

²RMCLs and WI PALs of 1.22. (1 mg/L=1.23 mg/kg of tire chips)

³The liquid concentrations are converted to mass of compound per kg of tire chips based on the given quantities of tire chips and liquid used in the study.

⁴Concentrations for compounds are taken from approximately 16 hour readings which are usually the highest concentrations achieved during the test. The liquid concentrations are converted to mass of compound per kg of tire chips based on the given quantities of tire chips and liquid used in the study.

⁵Concentrations for compounds are the final concentrations reached in 800 days. The liquid concentrations are converted to mass of compound per kg of tire chips based on the given quantities of tire chips and liquid used in the study.

with the highest concentrations) are not classified as hazardous metals in TCLP ¹⁸ limits. Concentration of arsenic exceeded Wisconsin PALs, but not RMCLs, in the study by Miller and Chadik (1993). In contrast, arsenic was not detected in the RMA (1990) study. The concentrations of barium reported by Grefe (1989), MCPA (1990), and Kim (1995) were below RCMLs but above Wisconsin PALs. Iron concentration reported in the MCPA (1990) study is the highest concentration obtained at the "worst case" condition (i.e., pH=3.5).

Although inorganic and organic compounds are found in tire chip leachates, they are generally below TCLP limits and are not significantly greater than USEPA's RMCLs and Wisconsin PALs, regardless of differences in the test conditions. It is also important to consider that in many studies the extraction liquid or test setup is designed for "worst case" conditions that do not necessarily exist in the environment that tire chips are used. For example, laboratory tests performed under stagnant conditions or tire chips exposed to aggressive extractions do not simulate conditions likely to exist in a tire chip embankment. Thus, in the field, lower concentrations are likely to exist. In fact, in results of two field studies, (MPCA 1990, Humphrey and Katz 1995), tire chips were found to have no significant effect on groundwater quality.

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